UDC 547-311

EPOXIDATION OF ALLYL ALCOHOL TO GLYCIDOL WITH HYDROGEN PEROXIDE AT TITANIUM SILICALITE

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It was studied the epoxidation mechanism of allyl alcohol using titanosilicate zeolite (TS-1) at 40°C by means of procedures for the nomination and discrimination of mechanism hypotheses. The hypotheses was carried out using the literature data and the preliminary experiment results. Discrimination hypothetical mechanisms implemented on the basis of the univariate results of the kinetic experiment, varying concentrations of allyl alcohol, hydrogen peroxide and glycidol. The most probable mechanism involves the hydrogen peroxide and allyl alcohol adsorption at the catalyst active centers and the glycidol formation at a reversible stage in the interaction of the adsorbed molecules of the reactants. Considered hypotheses include a different sequence of interaction of the reactants with active catalyst center. In addition, hypotheses take into account the formation of intermediate compounds as well as inactive products of the interaction of substances present in the reaction system, with the active centers on the silicalite surface. For each hypothesis, it was formulated the corresponding system of differential equations and carried out the estimation of the rate constants. The quality of the experimental data description was judged by the residual sums of squared deviations and correlation coefficients. The best results are obtained for the hypothesis involving the hydrogen peroxide and allyl alcohol adsorption at the two active catalyst centers with subsequent interaction of the resultant intermediates between them, with the formation of glycidol adsorbed on one center, free catalyst centre and molecule of water. Formation of free glycidol occurs at a reversible stage. A significant part of the active centers of the catalyst increasing the concentration of glycidol is associated with it. This is the main reason for the decrease of the reaction rate, apart from reducing the concentration of the reactants.

Keywords: *kinetics, mechanism, epoxidation, hydrogen peroxide, allyl alcohol, glycidol, catalysis, catalyst TS-1.*

Introduction

Oxygen-containing heterocyclic compounds (olefin oxides, cyclic acetals etc.) are important products and intermediates of heavy and fine organic synthesis [1–3]. Glycidol – allyl alcohol oxide – is of great practical interest. It is a valuable intermediate in the production of surfactants, plasticizers, textile dyes, photochemicals, pharmaceuticals, pesticides, a number of rubbers, varnishes, thermosetting resins and plastics [4].

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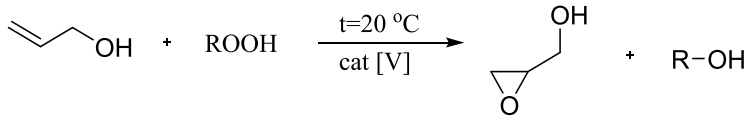
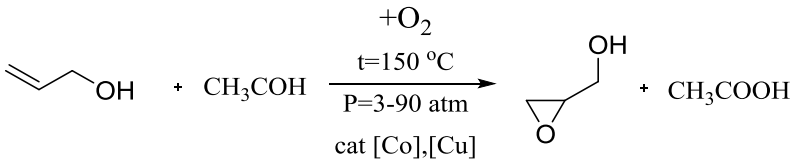
The main methods for preparing glycidol were developed back in 1950s [5–8]. Nowadays methods for preparing α-оксидов are mostly based on epoxidation of unsaturated compounds with hydrocarbon hydroperoxides and with peroxycarboxylic acids. A method for preparing glycidol by epoxidation of allyl alcohol with organic hydroperoxides in the presence of catalysts – inorganic compounds of vanadium [9] – was developed:

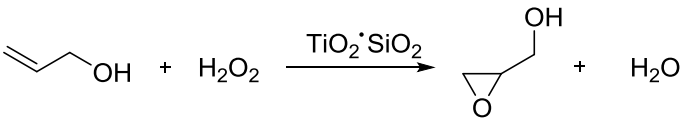


Because the chlorohydrin method and methods with the use of organic hydroperoxides are technologically complex and have shortcomings, more and more works devoted to looking for new economic methods of obtaining the above products are being published. A large part of these studies is focused on studying the possibility of oxidizing unsaturated compounds by oxygen with the formation of α-oxides:



In addition to the rather low characteristics of the process its essential shortcoming is that the reaction mass is a multicomponent mixture of oxidation products extremely difficult to separate. So, this method is not used in the industry.

Obtaining α-oxides by the oxidation of unsaturated compounds with molecular oxygen at "room conditions" remains most preferable. At the same time methods for obtaining olefin oxides based on the use of a second "green" oxidizer, hydrogen peroxide, are being developed. Thus, there is a series of works, in particular [10], devoted to obtaining glycidol by direct epoxidation of allyl alcohol with hydrogen peroxide in an organic solvent on a heterogeneous catalyst – titanium-containing zeolite TS-1:

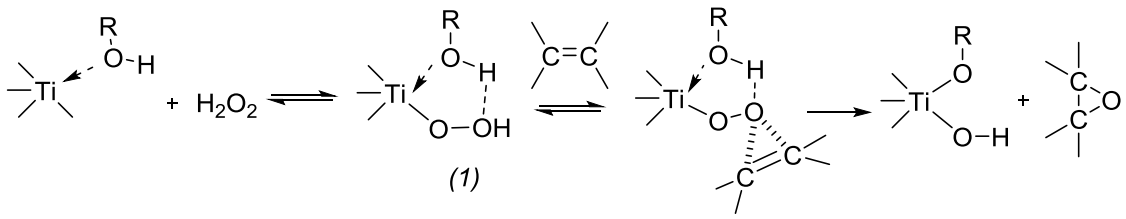


The molar ratio of alcohol and hydrogen peroxide is about 1:1, and the content of the catalyst in the reaction mixture is about 0.1% mass. A distinctive feature of this process is that it occurs at moderate temperatures and low pressures. Besides, it is attractive from the ecological viewpoint. The life duration of the titanium-containing silicalite is several times higher than that of the tungstate contact catalyst [10]. However, a shortcoming of this contact catalyst is the small

particle size. Having faced this problem, a group of authors [11] developed an improved catalyst form by transforming it into granules.

The heterolytic mechanism of TS-1 catalyst effect is considered to be most probable. It is analogous to the mechanism of the effect of peroxy acid, in which the key role is played by the electrophilic attack of the alkene double bond by the oxygen of the hydroperoxide group bonded with titanium [12]. It was shown that when hydrogen peroxide interacts with TS-1, hydroperoxide groups bonded with titanium are formed [13]. It is supposed that a distinctive feature of TS-1 catalyst as compared to other alkene epoxidation catalysts based on compounds of metals of groups IV–VI of the periodic system is the influence of the crystal structure of zeolite type characteristic of TS-1. Each active center is located in a channel about 0.55 nm in diameter. For this reason sterical hindrances are formed, because of which branched and cyclic alkenes react much slower than α-alkenes, and the probability of side transformations both of the initial alkene and of the formed epoxide significantly decreases.

Article [14] discusses a probable mechanism of epoxidation with the participation of TS-1. Besides, it presents possible structures of intermediates. Analyzing information on the influence of the nature of the solvent, acids and bases, data on the relative reactivity of alkenes of various structures the authors came to a conclusion that the most probable mechanism includes steps of the formation of intermediate 1 and its transformations upon interaction with the alkene. The discussion was carried out without quantitative data [14].



In later work [15] discrimination of three mechanisms of epoxidation of propylene is carried out on the basis of kinetic data (Z is the active site of the catalyst, P is propylene oxide):

1. $Z + ROH \rightleftharpoons Z{\cdot}ROH$
   $Z{\cdot}ROH + H_2O_2 \rightleftharpoons Z{\cdot}ROH{\cdot}H_2O_2$
   $Z{\cdot}ROH{\cdot}H_2O_2 + C_3H_6 \longrightarrow Z{\cdot}ROH{\cdot}P + H_2O$
   $Z{\cdot}ROH{\cdot}P \rightleftharpoons Z{\cdot}ROH + P$

2. $Z + ROH \rightleftharpoons Z{\cdot}ROH$
   $Z{\cdot}ROH + C_3H_6 \rightleftharpoons Z{\cdot}ROH{\cdot}C_3H_6$
   $Z{\cdot}ROH{\cdot}C_3H_6 + H_2O_2 \longrightarrow Z{\cdot}ROH{\cdot}P + H_2O$
   $Z{\cdot}ROH{\cdot}P \rightleftharpoons Z{\cdot}ROH + P$

3. $Z + ROH \rightleftharpoons Z{\cdot}ROH$

$Z{\cdot}ROH + H_2O_2 \rightleftharpoons Z{\cdot}ROH{\cdot}H_2O_2$

$Z{\cdot}ROH + C_3H_6 \rightleftharpoons Z{\cdot}ROH{\cdot}C_3H_6$

$Z{\cdot}ROH{\cdot}H_2O_2 + Z{\cdot}ROH{\cdot}C_3H_6 \longrightarrow Z{\cdot}ROH{\cdot}P + Z{\cdot}ROH + H_2O$

$Z{\cdot}ROH{\cdot}P \rightleftharpoons Z{\cdot}ROH + P$

Based on statistical criteria, mechanism 1 [15] including the adsorption of hydrogen peroxide and formation of the product as a result of attack of propylene to the oxygen atom of the peroxide group (Eley-Rideal mechanism) is considered to be most probable. It should be noted that according to the data presented in the specified article it is difficult to judge the quality of the experimental data description: the values of the correlation coefficients of are small (in case of the best mechanism – 0.92), and there is no comparison of the calculated and experimental data. Besides, the considered hypotheses obviously do not exhaust the number of possible mechanisms.

The kinetics of allyl alcohol epoxidation with the use of TS-1 was studied in [10, 16] to solve applied tasks. The process mechanism is practically not discussed in these works.

Thus, in publications known to us there is no information on the detailed mechanism of alkenes epoxidation with hydrogen peroxide on TS-1 catalyst. For this reason the purpose of this work was to determine the kinetics and mechanism of allyl alcohol epoxidation on TS-1 catalyst, which is now one of the best catalysts for alkenes epoxidation.

Experimental

Kinetic experiments were made in a glass static thermostated reactor with a reflux condenser at 40 °C and stirring of the reaction system with the use of a magnetic stirrer. The particle size of TS-1 catalyst and the chosen stirring intensity provided the course of the process in the kinetic area [11, 16].

Analysis of the contact solution composition was carried out by gas chromatography with the use of ethyl benzoate as an internal standard. Analysis conditions: glass nozzle column 3 m long, 3 mm in diameter; chromatographic phase: 3% of OV-17 on Chromatone N-Super; carrier gas: helium (2.1 l/h); evaporator temperature: 270 °C, temperature of columns thermostat: 160 °C; temperature of detectors thermostat: 180 °C; detector: catharometer. In all experiments solution volume was 7.5 ml, catalyst mass was 0.1 g.

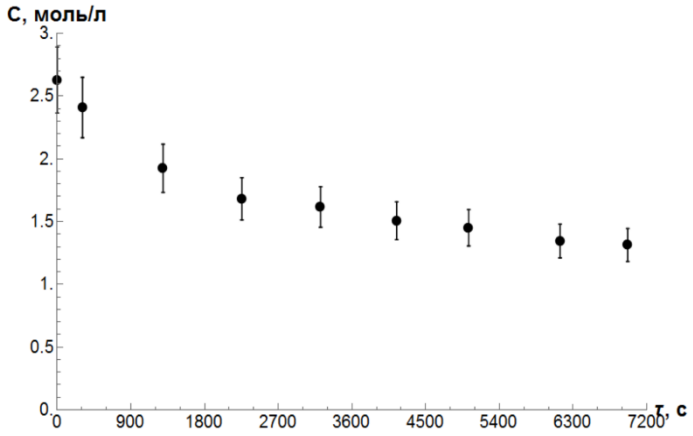
Methanol (chemically pure grade) was used as a solvent. When varying the initial concentration of allyl alcohol ("Acros", 99%), hydrogen peroxide ("ChemMed", state standard specification 177-88, hydrogen peroxide content: 33.7%), glycidol ("Acros", 97%), the solvent volume was changed, and the same initial concentration of the other reagents was maintained.

During experiments samples of the liquid phase were taken for chromatographic analysis and iodimetric titration to determine the content of organic compounds and hydrogen peroxide, respectively.

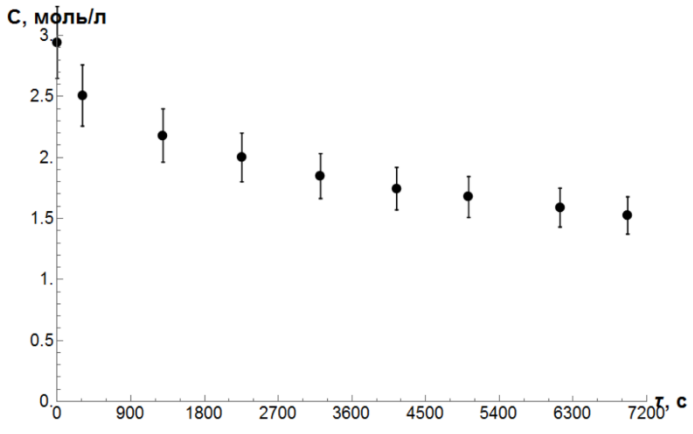
Kinetic data "concentration-time" were processed by means of "Kinetics" software package intended for solving primal and inverse problems of chemical kinetics, and also chemical equilibrium problems [17].

Results and Discussion

Kinetic regularities of allyl alcohol epoxidation were studied by the method of single-factor experiment at varied initial concentrations of hydrogen peroxide, allyl alcohol and glycidol. Results obtained in a typical experiment are presented in Figure 1.



a



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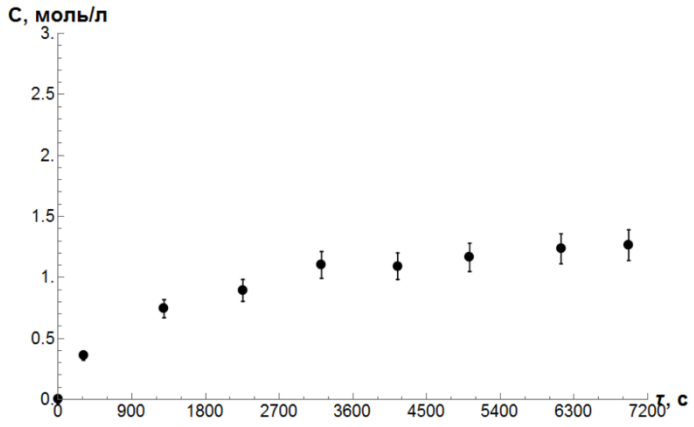
(Figure 1)



c

Figure 1. Changes in the concentrations of allyl alcohol (a), hydrogen peroxide (b) and glycidol (c) in a typical kinetic experiment.

[моль/л means mol/l]

The kinetic data were processed with the use of hypothetical mechanisms formulated on the basis of literature data and data of a preliminary experiment.

When forming a set of hypotheses, the following assumptions were made:

1. Glycidol is formed by the interaction of hydrogen peroxide with allyl alcohol on the active center of TS-1 catalyst.

2. The interaction of hydrogen peroxide and allyl alcohol with the active center can occur in any sequence. The first reagent is adsorbed (coordinated) by the active center. The second one can be adsorbed on the same or another similar center, or it can interact with the first reagent from the bulk (Eley-Rideal mechanism). Besides, Langmuir-Hinshelwood mechanism (interaction of molecules of the reagents bonded with the same centers or with two centers of TS-1 catalyst) is also possible.

Decrease of epoxidation rate at increasing concentration of the reagents and of glycidol is due to bonding of a part of active centers into intermediates or into inactive surface compounds. The set of considered hypotheses is presented in Table 1.

Table 1. Hypothetic mechanisms of allyl alcohol epoxidation

Mechanism 1		Mechanism 8	
1	$X_0 + HP \rightleftarrows X_1$	1	$X_0 + HP \rightleftarrows X_1$
2	$X_1 + AA \rightarrow GD + H_2O + X_0$	2	$X_1 + AA \rightarrow H_2O + X_4$
		3	$X_4 \rightleftarrows GD + X_0$
Mechanism 2		Mechanism 9	
1	$X_0 + AA \rightleftarrows X_2$	1	$X_0 + AA \rightleftarrows X_2$
2	$X_1 + HP \rightarrow GD + H_2O + X_0$	2	$X_1 + HP \rightarrow H_2O + X_4$
		3	$X_4 \rightleftarrows GD + X_0$
Mechanism 3		Mechanism 10	
1	$X_0 + HP \rightleftarrows X_1$	1	$X_0 + HP \rightleftarrows X_1$
2	$X_0 + AA \rightleftarrows X_2$	2	$X_0 + AA \rightleftarrows X_2$
3	$X_1 + AA \rightarrow GD + H_2O + X_0$	3	$X_1 + AA \rightarrow H_2O + X_4$
4	$X_1 + HP \rightarrow GD + H_2O + X_0$	4	$X_2 + HP \rightarrow H_2O + X_4$
		5	$X_4 \rightleftarrows GD + X_0$
Mechanism 4		Mechanism 11	
1	$X_0 + HP \rightleftarrows X_1$	1	$X_0 + HP \rightleftarrows X_1$
2	$X_1 + AA \rightleftarrows X_3$	2	$X_1 + AA \rightleftarrows X_3$
3	$X_3 \rightarrow GD + H_2O + X_0$	3	$X_3 \rightarrow H_2O + X_4$
		4	$X_4 \rightleftarrows GD + X_0$
Mechanism 5		Mechanism 12	
1	$X_0 + AA \rightleftarrows X_2$	1	$X_0 + AA \rightleftarrows X_2$
2	$X_2 + HP \rightleftarrows X_3$	2	$X_2 + HP \rightleftarrows X_3$
3	$X_3 \rightarrow GD + H_2O + X_0$	3	$X_3 \rightarrow H_2O + X_4$
		4	$X_4 \rightleftarrows GD + X_0$
Mechanism 6		Mechanism 13	
1	$X_0 + HP \rightleftarrows X_1$	1	$X_0 + HP \rightleftarrows X_1$
2	$X_0 + AA \rightleftarrows X_2$	2	$X_0 + AA \rightleftarrows X_2$
3	$X_1 + AA \rightleftarrows X_3$	3	$X_1 + AA \rightleftarrows X_3$
4	$X_2 + HP \rightleftarrows X_3$	4	$X_2 + HP \rightleftarrows X_3$
5	$X_3 \rightarrow GD + H_2O + X_0$	5	$X_3 \rightarrow H_2O + X_4$
		6	$X_4 \rightleftarrows GD + X_0$
Mechanism 7		Mechanism 14	
1	$X_0 + HP \rightleftarrows X_1$	1	$X_0 + HP \rightleftarrows X_1$
2	$X_0 + AA \rightleftarrows X_2$	2	$X_0 + AA \rightleftarrows X_2$
3	$X_1 + X_2 \rightarrow GD + H_2O + 2X_0$	3	$X_1 + X_2 \rightarrow X_4 + H_2O + X_0$
		4	$X_4 \rightleftarrows GD + X_0$

Designations: AA – allyl alcohol, HP – hydrogen peroxide, GD – glycidol, Z – catalyst active center, $X_0 \equiv Z$, $X_1 \equiv Z \cdot HP$, $X_2 \equiv Z \cdot AA$, $X_3 \equiv Z \cdot HP\ AA$, $X_4 \equiv Z \cdot GD$.

It follows from the analysis of the hypothetical mechanisms that discrimination of the hypotheses and identification of the most probable mechanisms requires studying the kinetic regularities at varied initial concentrations of the reagents and of glycidol.

The conditions of the made experiments are presented in Table 2.

Table 2. Initial concentrations of substances in experiments

No	AA	HP	GD	Water	Methanol	Cat.	Z*
	mol/l	mol/l	mol/l	mol/l	mol/l	g/l	mol/l
1	5.27	1.470	0	5.46	10.72	13.57	0.00537
2	5.27	0.499	0	1.852	12.89	13.53	0.00535
3	5.27	0.986	0	3.66	11.80	13.58	0.00537
4	5.29	1.960	0	7.28	9.64	13.52	0.00535
5	5.26	2.95	0	10.96	7.49	13.51	0.00534
6	0.871	2.95	0	10.94	15.89	13.63	0.00539
7	3.96	2.94	0	10.92	10.01	13.55	0.00536
8	1.756	2.94	0	10.91	14.21	13.47	0.00533
9	3.52	2.95	0	10.96	10.83	13.65	0.00540
10	4.40	2.95	0	10.97	9.15	13.52	0.00535
11	2.63	2.94	0	10.93	12.55	13.49	0.00534
12	5.98	2.47	0	9.16	8.56	13.52	0.00535
13	5.26	2.94	0.800	10.92	6.21	13.65	0.00540
14	5.25	2.96	0.406	11.00	6.82	13.54	0.00536
15	5.27	2.95	1.206	10.95	5.52	13.68	0.00541
16	1.494	1.475	0	5.48	18.29	13.61	0.00538
17	1.497	1.476	0	16.29	13.47	13.61	0.00538
18	1.495	1.470	0	21.6	11.09	13.74	0.00543

* The initial concentration of active centers Z is taken to be equal to the conditional concentration of titanium atoms in the solution based on the assumption that the content of TiO_2 in the catalyst is 3.16%.

The results of estimation of constants for the hypothetic mechanisms presented in Table 1 are shown in Table 3.

Table 3. Results of statistical analysis (best approximations) obtained for the hypothetical mechanisms (Table 1)

Model (mechanism)	p	S	R^2_{adj}
1	3	3.189	0.904
2	3	3.191	0.904
3	6	2.497	0.936
4	5	2.829	0.943
5	5	2.829	0.943
6	10	2.323	0.947
7	5	3.096	0.924
8	5	1.434	0.972
9	5	1.350	0.976
10	8	1.176	0.981
11	7	1.437	0.972
12	7	1.354	0.976
13	12	1.181	0.981
14	7	1.078	0.982

$S = \sqrt{\frac{\sum_{i=1}^{N}\left(\frac{y_{ei}-y_{ci}}{\sigma_i}\right)^2}{N-p}}$, $R^2 = 1 - \frac{\sum_i^N (y_{ei}-y_{ci})^2}{\sum_{i=1}^{N}(y_{ei}-\overline{y_e})^2}$, $R^2_{adj} = 1-(1-R^2)\frac{N-1}{N-p}$, $\overline{y_e} = \frac{\sum_{i=1}^{N} y_{ei}}{N}$,

where is S standard error; R^2_{adj} is corrected determination coefficient; y_{e_i} is the experimental value of response; y_{c_i} is the value of response calculated with the use of the model; $\overline{y_e}$ is the average value all of responses; σ_i is the standard error of measuring response y_{e_i}; N is the total number of measured values of responses; p is the number of varied parameters for this model.

It follows from the presented data that it is possible to describe experimental data with an error corresponding to the experiment error in case of mechanism No 14 (Langmuir-Hinshelwood mechanism). Standard deviation slightly exceeds 10% experimental error in case of Eley-Rideal type mechanism (No. 10). The calculated values of observed constants in case of two most probable mechanisms are presented in Table 4. It should be noted that all the constants are significant, i.e., no steps in these mechanisms can be neglected.

Table 4. The values of rate constants in case of the best approximations obtained for mechanisms 10 and 14

Mechanism 10

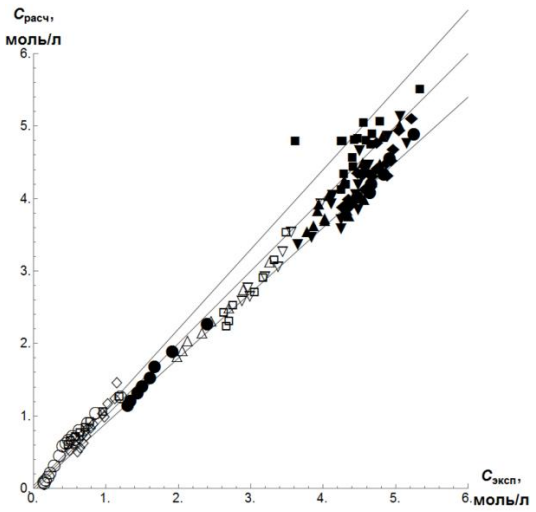
Parameter	Calc. value	Dimension
k_1	7.23×10^{3}	l/(mol·s)
k_{-1}	7.71×10^{-2}	1/s
k_2	7.97×10^{3}	l/(mol·s)
k_{-2}	8.07×10^{3}	1/s
k_3	1.80×10^{-1}	l/(mol·s)
k_4	9.09×10^{3}	l/(mol·s)
k_5	6.72×10^{2}	1/s
k_{-5}	4.12×10^{8}	l/(mol·s)

Mechanism 14

Parameter	Calc. value	Dimension
k_1	7.66×10^{1}	l/(mol·s)
k_{-1}	4.35×10^{2}	1/s
k_2	2.11×10^{1}	l/(mol·s)
k_{-2}	3.99	1/s
k_3	5.87×10^{6}	l/(mol·s)
k_4	9.62×10^{-1}	1/s
k_{-4}	8.36×10^{2}	l/(mol·s)

k_i and k_{-i} are rate constants of the direct and reverse reactions, respectively, at *i*-th step.

Quite good agreement of the calculated and experimental values of the reagents and glycidol concentrations (for the two specified mechanisms) is illustrated by two graphs "calculated concentrations – experimental concentrations" (Figure 2 – mechanism 10, Figure 3 – mechanism 14).



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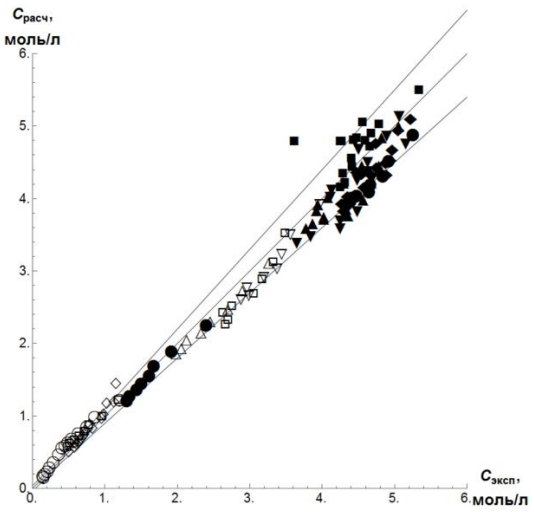
(Figure 2)



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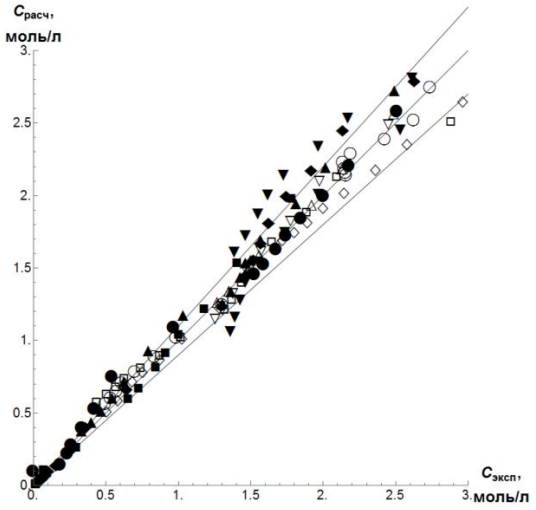

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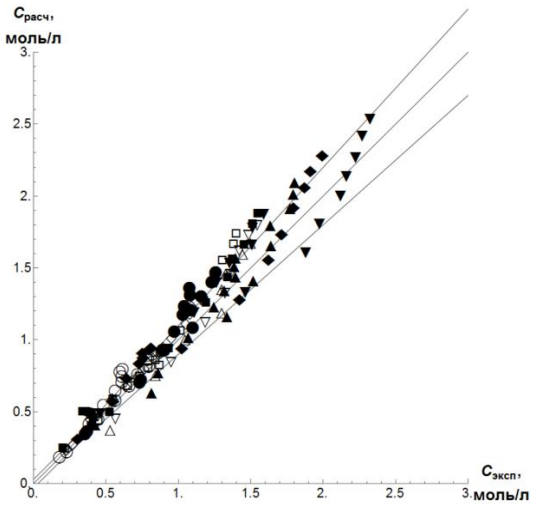

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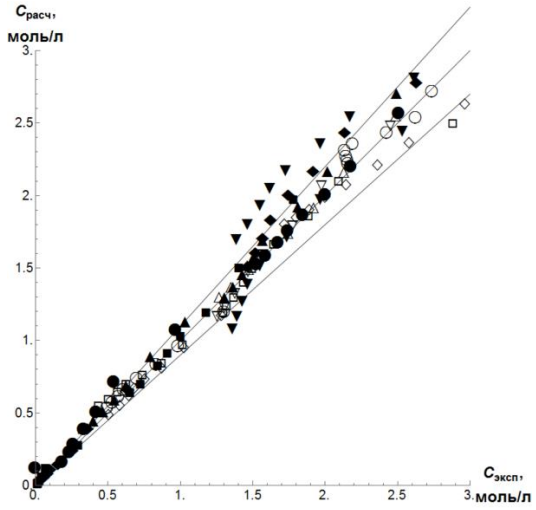
Figure 2. Agreement of calculated and experimental concentrations of allyl alcohol (a), hydrogen peroxide (b) and glycidol (c) for all experiments, mechanism 10.



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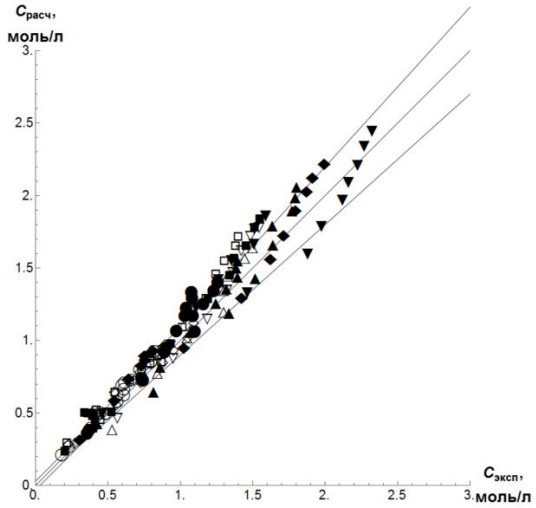

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Figure 3. Agreement of calculated and experimental concentrations of allyl alcohol (a), hydrogen peroxide (b) and glycidol (c) for all experiments, mechanism 14.

[$c_{расч}$ means c_{calc}; моль/л means mol/l; $c_{эксп}$ means c_{exp}]

The obtained results show that regularities of changing the concentrations of the reagents and main product in the course of allyl alcohol epoxidation with hydrogen peroxide on titanium-containing silicalite TS-1 at various initial concentrations of the reaction participants can be well described by Langmuir-Hinshelwood mechanism including non-equilibrium adsorption of hydrogen peroxide and allyl alcohol on adjacent centers of the catalyst and their interaction with each other with the formation of adsorbed glycidol (hypothesis No. 14, Table 1). It should be noted that the description of experimental data obtained in case of mechanism 10 including two routes of glycidol formation is almost as good as in case of mechanism 14. The first route includes adsorption of hydrogen peroxide and interaction of the peroxide group with allyl alcohol

from the bulk. The second route consists of allyl alcohol adsorption and interaction of hydrogen peroxide with it from the bulk with the formation of adsorbed allyl alcohol. This mechanism is less plausible, although there is no data so far for its unconditional discrimination. An essential factor is the significant decrease of the reaction rate by the formed glycidol. Besides, it follows from the performed research that the adequate kinetic model of epoxidation should consider the decrease of glycidol formation rate and the reagents concentrations, i.e., the process includes bonding of the catalyst active centers not only with hydrogen peroxide, but also with allyl alcohol. Possible structures formed by titanium contained in the active center of TS-1 and by allyl alcohols were discussed in [18].

Thus, as a result of the conducted study an adequate kinetic model of allyl alcohol epoxidation into glycidol was developed, and the most probable mechanism was suggested on the basis of hypothesizing and discrimination of hypotheses. The mechanism includes adsorption of hydrogen peroxide and allyl alcohol on adjacent centers of the catalyst and their interaction with each other with the formation of adsorbed glycidol.

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